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14. ABSTRACT

This final technical report begins with the objective the project, followed by detailed technical reports on the new accomplishments and findings obtained in the project. They are presented in three sections: A. Potential Energy Surfaces of Ion-Molecule Reactions, B. Potential Energy Surfaces for Photochemical Reactions and Nonadiabatic Processes, and C. Other Elementary Reactions. The Publication List and Interactions/Transactions conclude the report.

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1. Objectives.

Understanding the mechanism, kinetics and dynamics of elementary gas phase reactions is one of the major goals of chemistry. Such knowledge is also essential to chemistry in atmosphere associated with the spacecraft-atmosphere interactions and to chemistry of combustion and air pollution processes, as well as to reaction mechanisms, rates, dynamics in connection to the development of efficient chemical laser systems. The objective of the proposed research is to provide qualitative and quantitative theoretical information concerning the potential energy surfaces that dictate how the gas phase elementary reaction should occur. Such information is not easily available without theoretical studies and is complementary to the information obtainable from experimental studies. The state-of-the-arts ab initio molecular orbital and density functional calculations is used for this purpose, supplemented with classical and quantum dynamics calculations. Most of the systems for which theoretical calculations were performed in the proposed research are ion-molecule reactions, energy transfer reactions and photochemical reactions that are relevant to upper and lower atmospheric chemistry and development of chemical laser systems, relevant to the interest of AFOSR. These reactions typically involve several electronic states and cascade through these states via nonadiabatic processes that take place in the vicinity of the seam of crossing between them. Therefore, several potential energy surfaces and the crossing characteristics were calculated at the same time. The reactions studied theoretically in this research were mostly chosen based on the experimental studies carried out by groups at Air Force Laboratories (Hanscom and Albuquerque) and by scientists supported by grants from AFOSR, and a substantial collaboration between theory and experiment was involved.

2. Accomplishments and New Findings.

A. Potential Energy Surfaces of Ion-Molecule Reactions

a. The mechanism of the ion-molecule reaction of O^+ (^4S) + C_2H_2.

Theoretical and experimental studies are performed to elucidate the low energy charge-transfer dynamics of the reaction, O^+ (^4S) + C_2H_2 ($X\ ^1\Sigma_g^+$) → O + $C_2H_2^+$. In particular, the role of the low-frequency acetylene bending modes (612 and 730 cm^{-1}) in promoting charge transfer was examined. High temperature guided-ion beam measurements are carried out over the energy range from near-thermal to 3 eV at 310 and 610 K. The charge-transfer cross sections are found to decrease up to 0.5 eV, to have a constant value at intermediate energies between 0.5 and 1.5 eV, and then to dramatically increase above a threshold of a spin-allowed process determined to be at 1.7 eV. A bending vibrational enhancement of ~8 is observed at intermediate energies. Thermal energy rate coefficients are measured in a variable temperature-selected ion flow drift tube apparatus from 193 to 500 K. At each temperature, a negative energy dependence is observed. In order to elucidate the reaction mechanism in detail, high level ab initio calculations using Complete Active Space Self-Consistent Field (CASSCF) and Multi-Reference Single

and Double excitation Configuration Interaction (MRSDCI) methods have been performed. The results indicate that the charge transfer reaction occurs at an early stage via nonadiabatic transition between quartet and doublet states. There is a weak van der Waals minimum at the entrance channel between O^+ (^4S) and C_2H_2 with the relative energy of –1.51 kcal/mol. The minimum of the quartet/doublet crossing seam (Q/D MSX), where the spin-forbidden nonadiabatic transition is most likely to take place, lies very near this minimum at R_{CO} =4.06Å, R_{CC} = 1.20Å, and ∠CCH = 166.6° with a relative energy of -1.48 kcal/mol. After the nonadiabatic transition the system propagates on the doublet surface to reach the exothermic $O(^1D)$ + $C_2H_2^+(\tilde{x}\,^2\Pi_u)$ products. No energy barrier exists on the reaction pathway, strongly suggesting that the reaction should occur at low energy with a negative energy dependence, which is consistent with the experiment. The Q/D MSX has a bent acetylene moiety, which suggests that the excitation in bending modes will enhance the reaction, in agreement with the experiment.

The present work, performed in our group mainly by Kaori Fukuzawa, a visiting graduate student from Rikkyo University, Tokyo, has just been published as a joint paper between our group and two experimental groups at the Air Force Research Laboratory at Hanscom AFB, as K. Fukuzawa, T. Matsushita, K. Morokuma, D. J. Levandier, Y. Chiu, R. A. Dressler, E. Murad, A. Midey, S. Williams, and A. A. Viggiano, An ab initio and experimental study of vibrational effects in low energy O^+ + C_2H_2 charge-transfer collisions, J. Chem. Phys., **115**, 3184-3194 (2001). Another paper on the higher energy processes has been accepted for publication: K. Fukuzawa, T. Matsushita and K. Morokuma, *Ab initio* Potential Energy Surfaces of the Ion-Molecule Reaction: C_2H_2 + O^+, J. Chem. Phys., in press.

b. The mechanism of the ion-molecule reaction of O_2^+ + C_2H_2.

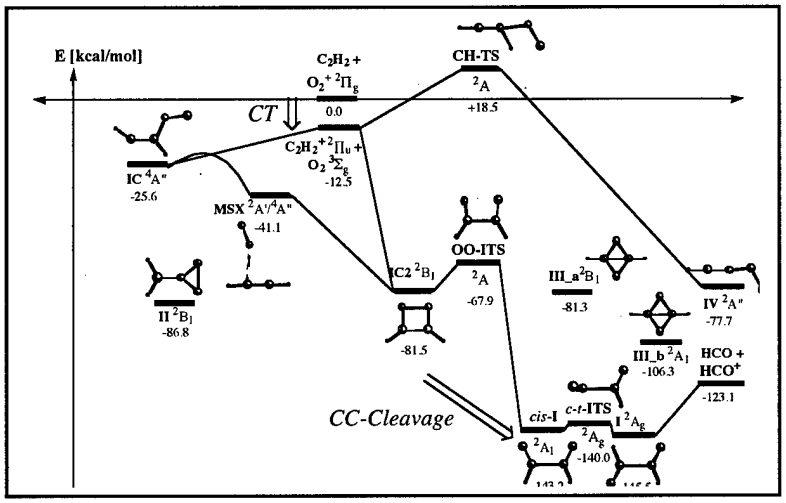
The reaction of acetylene with the molecular oxygen cation was studied at the Air Force Research Laboratory at Hanscom AFB [Y.-H. Chiu, R. A. Dressler, et al., J. Chem. Phys. **110**, 4296 (1999)]. It is one of many atmospheric reaction systems involved in partial kerosene combustion and therefore environmentally very important. In the experiments, guided ion-beam cross sections were measured and time-of-flight measurements were carried out. The following channels were observed for the C_2H_2 + O_2^+ reaction system:

1.) $C_2H_2^+$ + O_2 + 15.4 kcal/mol: Strong Charge Transfer (CT) channel

2.) Several weak exothermic complex channels leading mainly to HCO^+/COH^+, $C_2H_2O^+$, and CH_2^+ (COM)

The dominant reaction channel by far detected for all collision energies was $C_2H_2^+$ + O_2 (charge transfer channel, CT) and its associated cross sections was always two orders of magnitude larger than all COM channels combined. Even though the HCO^+/COH^+, $C_2H_2O^+$, and CH_2^+ channels are exothermic by up to 123 kcal/mol, they only appear after collision energy passes a threshold of approximately 10 kcal/mol. At high collision energies (200 kcal/mol and higher), HCO^+/COH^+ products reach a constant cross section value of ~ 1 $Å^2$ while the other products have declined.

We have carried out geometry optimization at the popular B3LYP/SVP density functional theory level, followed by frequency calculations and a G2-like high level energy correction using our modified G2MS in order to improve the energetics. The experimental geometry of acetylene and the best available theoretical geometry of $C_2H_2^+$ are reproduced within 0.01 Å for the bond lengths in the B3LYP/SVP calculations, as shown the following Figure. In particular we confirm that the ground state of $C_2H_2^+$ ($^2\Pi_u$) is a Renner-Teller Type A system where the two electronic states have just one common linear minimum. The lowest frequency at linear geometry is calculated to be 667 cm^{-1}. At infinite separation, the crossing between the reactant excited state asymptote O_2^+ ($^2\Pi_g$) + C_2H_2 ($^1\Sigma_g$) and the ground state asymptote O_2 ($^3\Sigma_g$) + $C_2H_2^+$ ($^2\Pi_u$) for the O-O stretch mode as well as for the C-C stretch coordinate occurs almost exactly at the bottom of the reactant PES. This finding explains readily why CT is orders of magnitude more dominant for all kinetic energies studied.



No long-range initial doublet complex was found that will allow the doublet intermediate ions to be formed by rearrangement. The absence of this complex is hence manifested in low cross sections for the COM channels. However, we located a minimum energy structure on the quartet surface, **IC**, which is able to connect to the doublet surface via a minimum on the seam of crossing, **MSX** (see Fig. 1). Once the doublet surface is reached, a highly exothermic channel leading eventually to the formation of HCO^+ is available via **IC2**. Only a small barrier exists to break the O-O bond in **IC2** to lead to the opened structure *cis*-**I**. Both *cis*- and *trans*-**I** minima exhibit a very long C-C bond of about 1.65 Å, which is likely to break due to the large exothermicity of this reaction. A minor channel was also detected via C-H insertion, which can take place in going over a 4-center transition state **CH-TS** at 18.5 kcal/mol that connects the CT products and $HCCOOH^+$ (**IV**). To confirm these reaction pathways, IRC calculations are currently carried out, and once they are completed, a manuscript will be prepared and submitted for publication before long. This study was mainly performed by Dr. Stephan Irle. A paper is in the final stage of preparation and will be submitted shortly.

c. Oxidation of alkyl ions, $C_nH_{2n+1}^+$ (n=1-5), in reactions with O_2 and O_3 in the gas phase.

The effects of ionization on hydrocarbon-air combustion chemistry are broadly applicable to a wide range of problems such as combustors for gas turbine engines, spark inhibition, improved engine performance, service life, explosion limits in blended fuels, hydrocarbon molecular growth, and ignition.

The oxidation of hydrocarbon ions in these environments is of fundamental interest. Rate constants and product ion branching fractions are reported for the reactions of CH_3^+, $C_2H_5^+$, s-$C_3H_7^+$, s-$C_4H_9^+$, t-$C_4H_9^+$, and t-$C_5H_{11}^+$ with O_2 and O_3 at 300 K in a variable temperature-selected ion flow tube (VT-SIFT). All of the ions listed above were found to show no reactivity, $k < 5x10^{-13}$ cm^3 s^{-1}, with O_2, despite the availability of reaction channels with exothermicities of several hundred kJ/mol. On the other hand, the reaction rate constant for CH_3^+ with O_3 is remarkably large. The $C_2H_5^+$, s-$C_3H_7^+$, and s-$C_4H_9^+$ ions are somewhat less reactive, reacting at approximately 7-46% of the thermal capture rate. The HCO^+ and $C_2H_3O^+$ ions are the major products in these reactions. The t-$C_4H_9^+$ and t-$C_5H_{11}^+$ ions are found to be unreactive with rate constants $< 5x10^{-12}$ cm^3s^{-1}, which is the present experimental detection limit.

We carried out geometry optimizations using Gaussian's implementation of the B3LYP hybrid density functional, using the standard 6-31G(d) basis set. Open shell fragments were treated using the spin-unrestricted density funcional formalism. Analytical frequency calculations were used to characterize the nature of these stationary points. All of the reaction pathways were verified by intrinsic reaction coordinate (IRC) calculations both forward and backward from the encountered TSs. Standard Mulliken population analysis was employed to analyze electron density and spin density distributions from the B3LYP/6-31G(d) densities. From these calculations, we draw the following five theoretical conclusions:

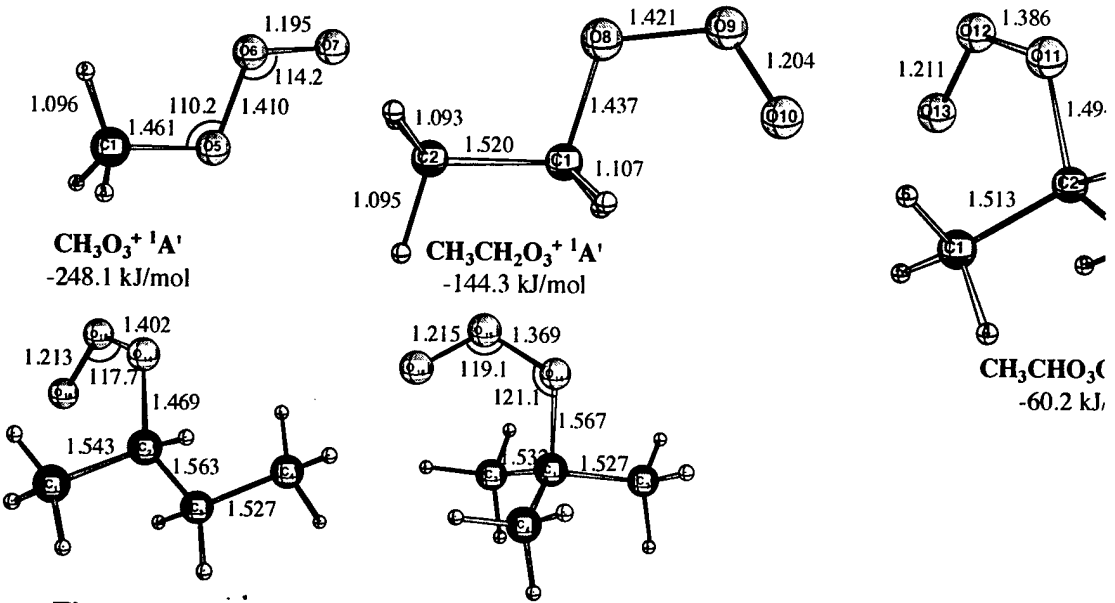


Figure 2: Initial reactant complexes for alkyl cations with ozone. Geometries were optimized at the B3LYP/6-31G(d) level of theory, bond distances are in [Å] and bond angles in [°]. Interaction energies are in [kJ/mol] with respect to isolated alkyl cations and ground state ozone.

1. The interaction of O_2 with alkyl cations only gives weak complexes with large C-O bond distances. The interaction is repulsive at smaller distances, and does not lead to reactions.

2. For the reactions of ozone with methyl cation, a very early O-O cleavage transition state with a low barrier of only 48 kJ/mol leads to the highly exothermic formation of HCO^+; This corresponds closely with the experimental high yield of this channel. It is unclear if H_2O_2 is formed in this channel.

3. The same channel will most likely exist for ethyl- and propyl-systems as well.

4. Similarity between *n*- and *i*-propyl reaction systems can be explained by barrierless (fast) rearrangement of *n*-propyl.

5. The trend toward lower reactivity with increasing order of the reactant carbocation can be explained by our finding that initial alkyl cation/ozone complexes are largely destabilized when alkyl groups are added to the cationic center.

This work was performed by Dr. Stephan Irle and Qingfang Wang, a graduate student, and is being prepared for publication.

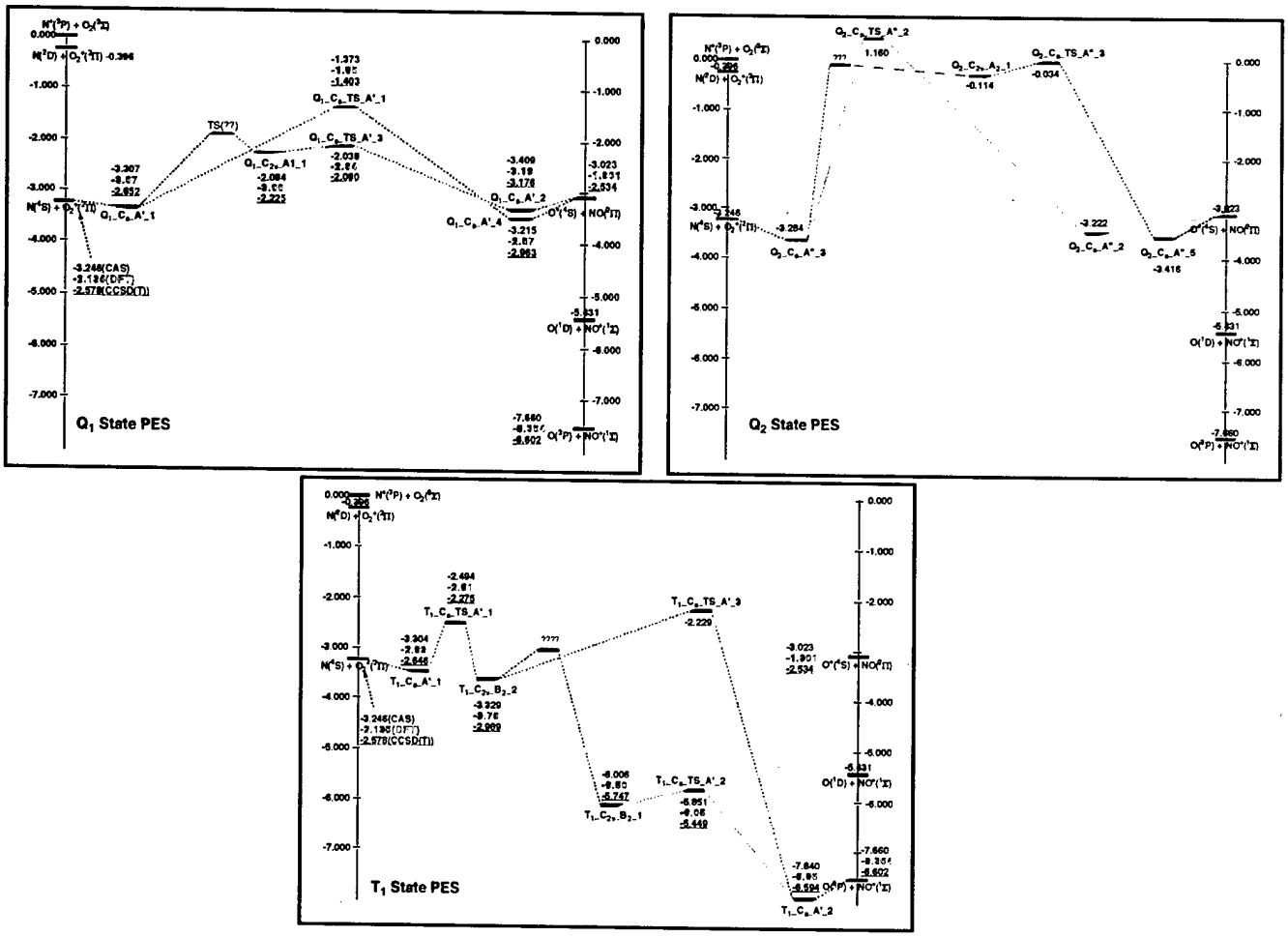
d. The mechanism of the ion-molecule reaction of $N^+(^3P) + O_2(^3\Sigma_g)$

The reaction of oxygen molecule with nitrogen cation has been recently studied by Air Force Research Laboratory at Hanscom AFB. It is one of the important reactions in controlling electron density in the ionosphere. Recent experiments using HTFA (high temperature flowing afterglow) and SIFT (selected ion flow tube) techniques indicated the following results:

$$N^+(^3P) + O_2(^3\Sigma_g) \rightarrow O^+(^4S) + NO(^2\Pi) \quad (<10\%) \quad \text{Product\_1}$$
$$O(^3P) + NO^+(^1\Sigma) \quad (\sim 40\%) \quad \text{Product\_2}$$
$$N(^4S) + O_2^+(^2\Pi) \quad (\sim 50\%) \quad \text{Product\_3}$$

None of the channels have strong energy dependence. But at high energy, drift tube measurements showed that the charge transfer and O^+ production became increasingly important. Since none of the products can correlate to the reactants based on the dominant electron configuration argument, non-adiabatic transition must occur in the reaction. The goal of present study is theoretically to clarify the reaction mechanism, calculate the rate constants and explain the experimental observations, such as the temperature dependence of charge transfer and O^+ products. We have used CASSCF(16e/12o)/cc-pVTZ, CCSD(T)/cc-pVDZ and B3LYP/cc-pVTZ methods for geometry optimization of the equilibrium, transition state, product for both overall quintet (Q_1, Q_2,) , triplet (T_1, T_2) states, singlet (S_1, S_2) states and the seam of crossing between Singlet and triplet or singlet and quartet or triplet and quartet.

Some results are shown in the following figures



These results indicate that reactions first go through charge transfer process to form $N(^4S)$ + $O_2^+(^2\Pi)$ product, and this process occur in the overall quintet state. From the figures, we can see that Q_2 potential surface (PES) is energetically in the vicinity of the PES of the reactants, therefore charge transfer reaction should occur between Q_2 and Q_3 PES. The reaction barrier on the Q_2 surface is quite high (~1.16eV), therefore the corresponding products must have small contribution. This results agree well with the experiment; the $O^+(^4S)$ + $NO(^2\Pi)$ product is less 10%. The other product, $O(^3P)$ + $NO^+(^1\Sigma)$, is formed through the triplet surface. In the ion-molecule complex region, the quintet and triplet PESs are extensively crossed, and therefore the reaction can also occur on triplet surfaces. Currently we are writing a paper to describe the potential energy surfaces calculations, and this will be finished very soon. Dr. Stephan Irle and Mr. Peng Zhang are mainly responsible to the calculations, and a joint paper with the experimental group at Hansom AFRL is being prepared.

B. Potential Energy Surfaces for Electronic Spectroscopy, Photochemical Reactions and Nonadiabatic Processes.

a. Symmetry Breaking and its Effect on the Potential Surface of NO_3.

The ground and excited electronic states up to approximately 100 000 cm^{-1} of the nitrate free radical (NO_3) are investigated by complete active space self-consistent-field (CASSCF) and multi-

reference–singles doubles configuration interaction calculations. Extended basis sets, containing polarization and diffuse functions, and an active space consisting of 13 orbitals and 17 electrons are used. A total of 28 electronic states is obtained within the D_{3h} framework which split into 44 states in C_{2v}. All calculated states are valence states and their character is discussed in detail. Oscillator strength and radiative lifetimes are determined from the CASSCF wave functions and give evidence for a strong transition that was not yet known experimentally. For the experimentally observed ^2E and ^2E states equilibrium geometries, harmonic frequencies, and adiabatic excitation energies are calculated in excellent agreement with experimental data. Important new insight is gained about the role of the low-lying electronic states in the photodissociation and the mechanism of this process is discussed.

This work, performed by Dr. Wolfgang Eisfeld, a postdoctoral fellow, has just been published as W. Eisfeld and K. Morokuma, Ab initio investigation of the vertical and adiabatic excitation spectra of NO_3, J. Chem. Phys., **114**, 9430-9440 (2001).

b. Theoretical study of the photoelectron spectrum of NO_3 and the excited states of NO_3^+.

The photoelectron spectroscopy of NO_3 is of considerable interest, particularly because of the radical's relevance in atmospheric chemistry, but recent studies gave controversial results. In the current study we present high-level ab initio calculations of the vertical and adiabatic electronic spectrum of NO_3^+ and the photoelectron spectrum of the radical. The vertical ionization spectrum up to 18~eV was calculated by complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MR-CI) methods, using extended basis sets. For D_{3h} geometries 15 ionic singlet and triplet states are found and characterized within this energy range of which only the lowest four are due to principal ionization. For geometries of lower symmetry these states split into 23 states of which seven correspond to principal ionizations. Equilibrium geometries and harmonic frequencies were computed for the controversial higher principal ionizations and adiabatic ionization potentials were obtained. These results disagree in several points with previous experiments and their interpretation.

This work is in press as W. Eisfeld and K. Morokuma, "Theoretical study of the photoelectron spectrum of NO_3 and the excited states of NO_3^+." in J. Chem. Phys., **114**, 9430-9440 (2001).

c. Excited Potential Energy Surfaces and Mechanism of Photodissociation of NO_3.

The photodissociation of NO_3 plays a significant role in atmospheric chemistry, particularly in the troposphere. NO_3 is a major player in the odd nitrogen and oxygen cycles and to a large extent is responsible for the night-time oxidation capacity in the troposphere. The photochemistry of NO_3 shows two dissociation channels.

$$NO_2\,(^2A_1) + O\,(^2P) \xleftarrow[\textbf{channel II}]{17033\ cm^{-1}} \boxed{NO_3} \xrightarrow[\textbf{channel I}]{16543\ cm^{-1}} NO\,(^2\Pi) + O_2\,(^3\Sigma_0^-)$$

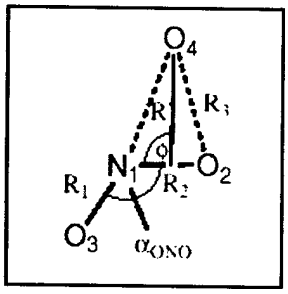
The mechanism poses a number of interesting and still unexplained questions. Particularly the close energetic vicinity of the two dissociation thresholds and the complete dominance of channel (II) when energetically accessible are important points to be studied.

The necessary treatment of excited states and the circumstance that we have to treat radical-radical product channels inevitably call for multi-reference *ab initio* methods. Preliminary results have be obtained by CASSCF calculations with 17e/13o or 15e/12o active spaces and extended basis sets. These calculations are not precise enough and have to be improved by MR-SDCI+Q calculations.

First the vertical and adiabatic excitation spectra of NO_3 were calculated with high accuracy and in very good agreement with experiments. Group theoretical analysis turns out that the bright $^2E'$ state is neither adiabatically nor diabatically connected to the two asymtotes for channels (I) and (II). In fact conical intersections are found between the $^2A_2$ state, arising from $^2E''$ by N---O bond stretching along a C_2 axis, with the $^2B_2$ and $^2A_1$ states that originate from $^2E'$.

On the lowest two potential surfaces of $^2B_2$ and $^2B_1$ symmetry, reaction (II) is a direct and barrierless process along a C_{2v} coordinate. The formation of products (I) is orbital-symmetry forbidden in C_{2v} and actually follows a C_s coordinate. The radical has to rearrange in order to form an O---O bond that would lead to the peroxo-nitrate, ONOO. However, our calculations show that ONOO is not a stable species. Thus the barrier to rearrangement is also the only reaction barrier for dissociation to products (I).

A special coordinate system has to be used to efficiently find the barrier of this reaction which is shown in the inset. So far only preliminary results were obtained at the MR-RS2 level of theory, which are currently improved by MR-SDCI calculations. It turns out that the transition structure shows an extremely long R' of far over 3 Å and that ϕ is around 90 deg. This corresponds to an O atom that is only weakly interacting with a NO C_2 fragment. Thus, as long as the excess energy is insufficient to reach the asymptote for direct dissociation, the only other reactive possibility is to cross the barrier to rearrangement. Due to the structure of the corresponding transition state, the energy is only slightly below the exit channel for (II) which is in excellent agreement with experimental findings. The TS also explains why no products of (I) can be found once channel (II) is open. There simply would be no force to cause the rearrangement, although (I) leads to thermodynamically much more stable products. This is a very satisfactory explanation of the observations. A paper has been published: W. Eisfeld and K. Morokuma, Ab initio investigation of the vertical and adiabatic excitation spectra of NO_3, J. Chem. Phys., **114**, 9430-9440 (2001).



d. On the potential stability of the peroxo nitrate radical (ONOO).

The existence of the peroxo nitrate radical (ONOO) is discussed since a long time and its mutual formation was used to explain the obscure scavenging process of NO_3 in the Earth's atmosphere. In this study we report our thorough investigation of the stability of this species by means of highly correlated ab initio calculations. Single-reference coupled-cluster singles and doubles (CCSD) as well as multi-

reference configuration interaction (MRCI) calculations were performed to optimize equilibrium structures and obtain harmonic force fields. The force fields were used to calculate the harmonic frequencies as well as isotopic shifts. The CCSD calculations result in shallow minima for both the $^2A''$ ground as well as the $^2A'$ excited state. However, the calculated isotopic shifts of the ground state show that the experimentally observed shift of 50 cm^{-1} cannot be due to ONOO. In contrast, no minima were found by the MRCI calculations. The analysis of the wave functions indicates that the potential wells obtained by CCSD are artifacts that are due to the single-reference nature of the CCSD method. Our conclusion is that ONOO is not a bound structure and cannot be observed experimentally. Our calculations also show that thermal decomposition of NO_3 into NO and O_2 is not possible under atmospheric conditions and thus this channel cannot be responsible for the unknown NO_3 scavenging process discussed in the literature.

Our high-level multi-reference calculations show that no stable doublet structure for the proposed ONOO radical exists. The finding of potential wells for this species by single-reference methods like CCSD is explained by the limitation of such methods to treat the spin couplings appropriately that occur during the bond breaking process. We also showed, based on such CCSD optimized equilibrium structures, that the isotopic shift of the NO stretching vibration is no experimental evidence for the existence of ONOO. Only isotopomeres containing the ^{18}ON--OO labeling would give the observed shift but this isotopic arrangement was ruled out in the experiments. Our findings have consequences for the interpretation of the NO_3 chemistry in the atmosphere. It was assumed that the formation of either stable ONOO or its fragmentation products NO and O_2 could explain the observed but obscure NO_3 scavenging process discussed in the literature. Our calculations show that this reaction channel is certainly not accessible at thermal energies under atmospheric conditions. First of all, this process would have to take place on the first excited state surface which would require an excitation energy of over 80 kJ/mol. Second, a substantial barrier would have to be overcome to reach the NO + O_2 exit channel. Both are in disagreement with the estimated barrier height of 51 kJ/mol for the unknown scavenging process. This means that the search for the unknown NO_3 scavenger needs to be focused into a different direction.

The present work was published as W. Eisfeld and K. Morokuma, Theoretical study of the potential stability of the peroxo nitrate radical (ONOO), J. Chem. Phys., **119**, 4682-4688 (2003).

e. Photodissociation of ClN_3

Production of electronically excited metastable species via direct chemical reaction is central to the development of short-wavelength chemical laser such as iodine laser [G. C. Manke, G. D. Hager, *J. Mod. Opt.* **49**, 465 (2002).]. NCl($a^1\Delta$) is one of this kind of metastable species. Furthermore, photolysis of ClN_3 has been used as a convenient source of NCl($a^1\Delta$) for kinetic measurements that are required for further development of this chemical laser. Unfortunately the present understanding of the primary photochemical dynamics of chlorine azide is incomplete.

Recent experimental studies[N. Hansen, A. M. Wodtke, A. V. Komissarov, M. C. Heaven, *Chem. Phys. Lett.* **368**, 568 (2003)] suggested both spin-allowed and spin-forbidden channels. Also, in the UV photolysis of ClN_3 near 203 nm,

$$ClN_3 + h\nu \rightarrow NCl(a^1\Delta) + N_2(X^1\Sigma_g^+) \quad (1)$$

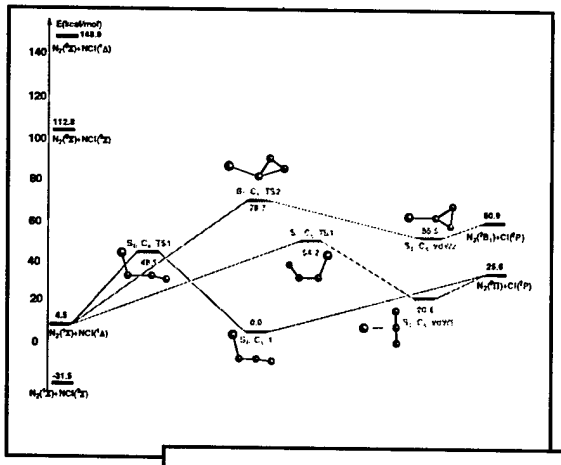
$$\rightarrow NCl(X^3\Sigma^-) + N_2(X^1\Sigma_g^+) \quad (2)$$

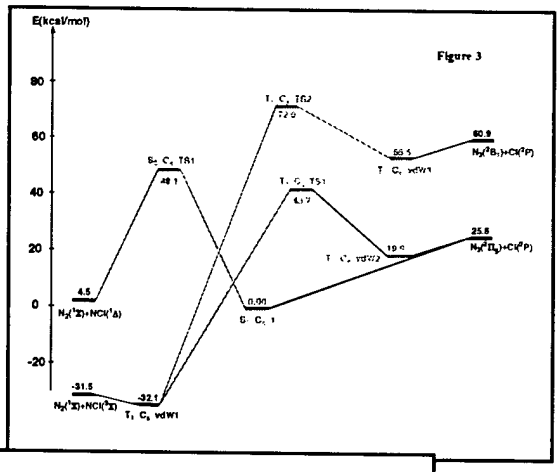
$$\rightarrow NCl(X^3\Sigma^-) + N_2(A^3\Sigma_u^+) \quad (3)$$

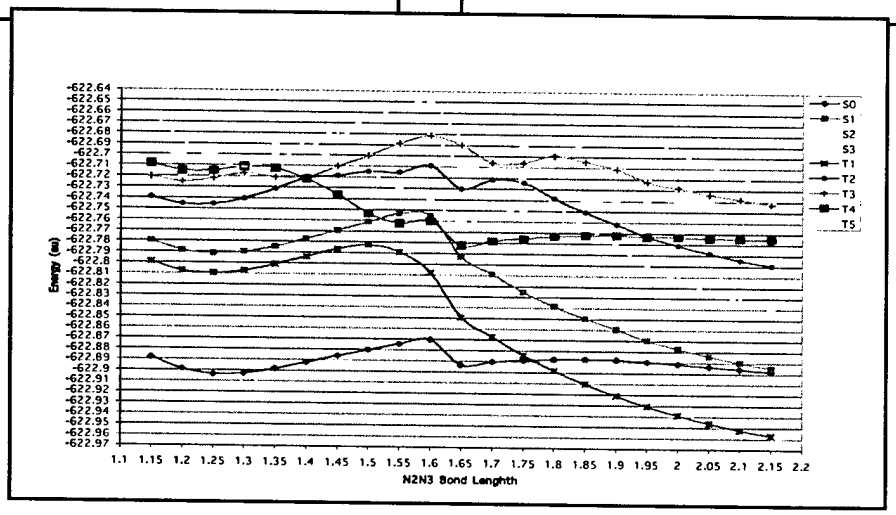
$$\rightarrow NCl(b^1\Sigma^+) + N_2(X^1\Sigma_g^+) \quad (4)$$

the singlet-triplet branching ratio of 0.78/0.22 was observed. With 203 nm laser, the ClN_3 could be excited to B or C state, but obviously, none of these states can correlate to the channel (1) or (2) products, potential-energy surface crossing is involved in the photodissociation dynamics. The goal of present study is theoretically to clarify the reaction mechanism and propose more efficient way to generate $NCl(a^1\Delta)$ product. Considering the multiconfiguartional nature of excited states, we have used CASSCF method for geometry optimization of both Singlet and triplet surfaces. At the same time, *ab initio* direct dynamics studies have been carried out to gain further insights into the photodissociation dynamics of excited states.

Some preliminary results are shown in the following figures.





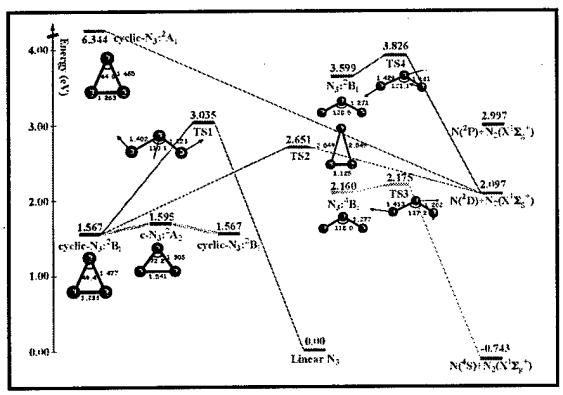


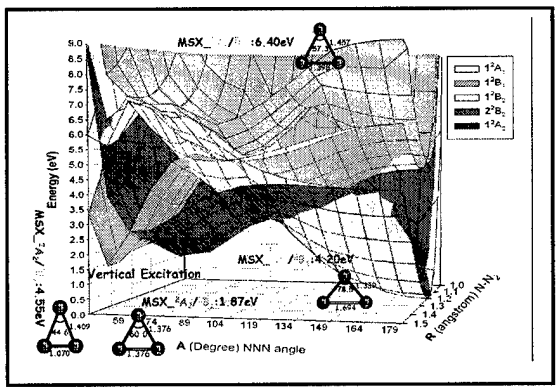
Basically, we have found that 8 states may contribute to the non-adiabatic photodissociation process, they are S_{0-3} and T_{1-4}. Also, we found the nature the three singlet excited states involves the electron transition from non-bonding orbitals to the mixture of NN π^* and NCl σ^* orbital. On the S_0 state, we have determined that the dissociation barrier (channel (1)) is about 40 kcal/mol. However, on the excited state surfaces, we have not found any minima besides some of the van de waals complex. To explain the non-adiabatic process, we have found a possible pathway, which go through two intersystem crossings (S_2/T_2 and S_1/T_2) and could lead the excited molecule to dissociate to the experimental observed products. But obviously, this may not be an efficient process, we proposed that direct internal conversion could be the leading factor, and other intersystem crossing processes could also contribute, the calculations concerning on this aspect is still in progress. Mr. Peng Zhang is mainly working on this project. The paper is in the final stage of preparation.

f. Photodissociation of cyclic N_3

Nitrogen cluster have received considerable attention as good candidate for high-energy density materials (HEDM). Their natural tendency to decompose to N_2 also makes them high on the list of environmentally friendly explosives and propellants. Cyclic N_3 is the smallest cluster of these species and is the only precursor to tetrahedral N_4 cluster. So study of this kind of system is obviously very important. Recently, Wodtke's group found strong evidence of photochemical production of cyclic N_3 in the velocity map imaging results on ClN_3 photochemistry.[N Hansen and A.M. Wodtke, private communication] However, there is no experiment concerning the means for photochemical formation of cyclic N_3; Also, there is no experiment, which could directly detect the cyclic N_3. Therefore, theoretical study would be very helpful in providing important information in experimental design and gaining much deeper insights into its photodissociation dynamics. We have performed CASSCF(15e/12o)/6-311+G(3df) method for geometry optimization of the equilibrium, transition states, products for both doublet (D) and quintet (Q) states and seam of crossings between those corresponding states.

Some preliminary results are shown in the following figures.





Basically, we have found, on the ground state, the cyclic N_3 dissociation barrier is about 1.4 eV within the C_{2v} symmetry, and the cyclic N_3 could also isomerize to linear N_3 with a barrier height of 1.6 eV. For comparison, we also calculated the dissociation barrier for the linear N_3 and found a 2.0 eV barrier. Before the cyclic N_3 C_{2v} dissociation transition state region, we have located the MSX (minimum of seam of crossing) between D_0 and Q_1 state, whose energy is about 0.2 eV lower than the dissociation transition state. Spin-orbit calculation showed that the norm of spin-orbit coupling matrix is about 40 cm^{-1}, which is significant for the light triatomic system. As a consequence, the electronic transition to the quartet surface would have a high probability. On the excited state, we found $^2A_1$ state, which is the state to be excited by 5 eV photon, is a very weakly bounded state, and its dissociation is almost a barrierless process. At the same time, we found several internal conversion and intersystem crossing pathways, which may bring the excited molecules down to the ground or other lower excited states and results in a very complicated dissociation or isomerization mechanisms. To clarify those complicated processes, we plan to construct the potential energy surfaces both for ground and excited states, and then run nonadiabatic dynamics. A joint paper with Prof. Wodtcke is in the final stage of preparation by Peng Zhang, a graduate student working on this project.

g. *Ab initio* molecular orbital study of the weak $\tilde{C}^2A' \leftarrow \tilde{X}^2A'$ transition of the vinyl radical.

Oscillator strength was calculated for the vinyl radical at MRCISD and CASSCF level between the ground state and several doublet excited states. Results indicate that the $\tilde{C}^2A' \leftarrow \tilde{X}^2A'$ transition, of $\pi^* \leftarrow \pi$ character that is usually thought to be strong, is indeed very weak. The $\tilde{C}^2A'$ state is the result of coupling between the $\pi^* \leftarrow \pi$ triplet excited configuration and the nonbonding electron and the $\tilde{C}^2A' \leftarrow \tilde{X}^2A'$ transition is essentially "spin-forbidden". Another high-energy doublet state is found with strong transition with the ground state arising from coupling between the $\pi^* \leftarrow \pi$ singlet state and nonbonding electron. This looks like a common feature for $\pi^* \leftarrow \pi$ excitation in σ radicals.

The present work was published as: P. Zhang and K. Morokuma, *Ab initio* molecular orbital study of the weak $\tilde{C}^2A' \leftarrow \tilde{X}^2A'$ transition of the vinyl radical, Chem. Phys. Lett., **367**, 482-488 (2003)..

h. Potential surfaces and mechanism of A state photodissociation of the vinyl radical.

The study of the electronic structure and the dynamics and mechanism of photodissociation reaction of free radical species is a hot subject. Concerning photodissociation of the vinyl radical, two groups have performed new experiments. Suit et al. [M. Ahmed, D. S. Peterka, A. G. Suits, J. Chem. Phys. **110**, 4248 (1999)] used the velocity map imaging technique to study vinyl photodissociation from the B and C states at 243nm excitation, which gave the following product channels.

B and C states $\rightarrow H_2CC(X\ ^1A')$ or C_2H_2 $(X\ ^1\Sigma_g^+)$, also C_2H_2 $(a\ ^3B_2)$+ H

Zhang et al. [K. Xu and J. Zhang, J. Chem. Phys. **111**, 3783 (1999); also private communication] used 327.4 and 366.2 nm excitation and the Rydberg atom time-of-flight technique to study photodissociation from the A state:

A state $\rightarrow C_2H_2\ (X\ ^1\Sigma_g^+)$ + H

They found inverted CC stretch & CH bend progressions in the product. They also measured a positive angular distribution β value at 327.4nm, but a negative value at 366.2nm.

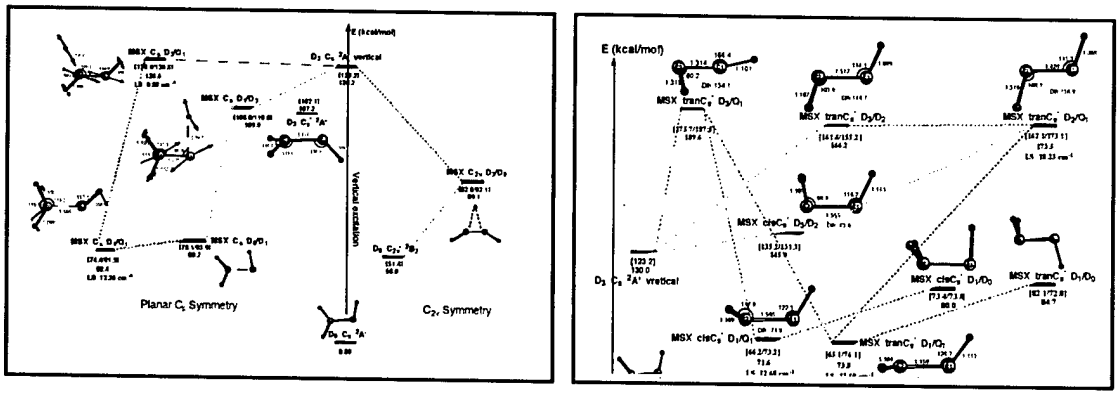
Complete active space self-consistent field (CASSCF) and multi-reference single and double excitation configuration interaction (MRSDCI) calculations have been carried out on potential energy surfaces of the vinyl radical to study photodissociation dynamics starting from the first excited doublet (D_1, $\tilde{A}$) state. Both internal conversion and intersystem crossing channels, which bring the excited vinyl radical down onto the ground state potential energy surface and dissociate, have been identified within planar C_s, twisted C_s and C_{2v} symmetry. The most efficient reaction channels are the direct internal conversion from D_1 and the ground state (D_0) within planar C_s symmetry, with an energy barrier height of ~80 kcal/mol (with respect to the ground state globe minimum), and the internal conversion from D_1 to D_0 within twisted C_s symmetry with the required energies of about 85.0 and 76.0 kcal/mol at the two minima of conical intersection respectively. Due to the small spin-orbit coupling between D_0-and the lowest quartet state (Q_1) or D_1 and Q_1 within twisted C_s and C_{2v} symmetry, the intersystem crossing channels are not efficient, and also these processes require high excitation energy.

The present work is just being submitted for publication as: P. Zhang, G. S. Tschumper, S. Irle and K. Morokuma, *Ab initio* theoretical studies of potential energy surfaces for the photodissociation of the vinyl radical. I. $\tilde{A}$ state dissociation, J. Chem. Phys., **119**, 6524-6538 (2003).

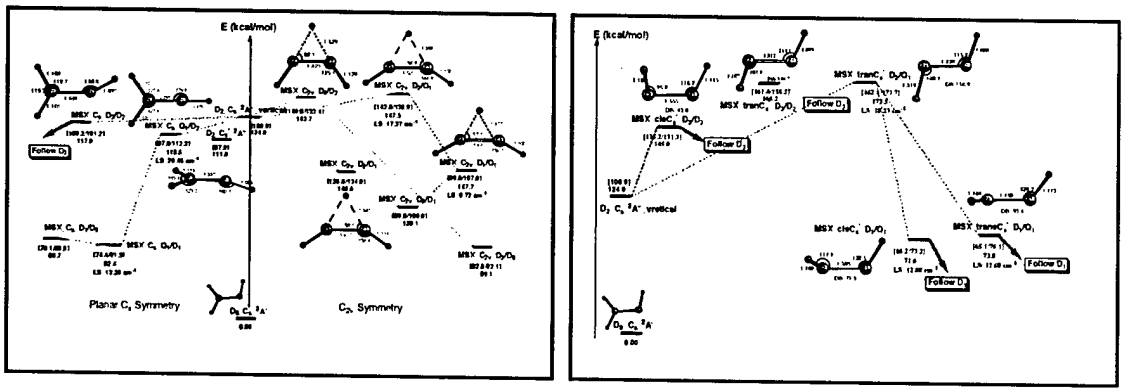
i. Photodissociation of the vinyl radical: B and C states

To study the photodissociation dynamics starting from the second doublet B (D_3) and C (D_2) states, complete active space self-consistent field (CASSCF) and multi-reference single and double excitation configuration interaction (MRSDCI) calculations have been carried out. Both internal conversion and intersystem crossing channels, which bring the excited vinyl radical down onto the ground state potential energy surface and dissociate, have been identified within planar C_s, twisted C_s and C_{2v} symmetry. More specifically, for the dissociation from C state, the internal conversions in planar C_s symmetry pathway (crossing between D_3 and D_1 state) is the most efficient nonadiabatic reaction channels, and its energy threshold is about 110 kcal/mol, which is lower than the photon excitation energy used in the experiment. The intersystem crossing pathway has little contribution because of small spin-orbit coupling between Quartet and D_3 state. Although C_{2v} internal conversion pathway has a lower energy requirement (~90 kcal/mol), the initial vibrational excitation is necessary to promote the

corresponding vibrational modes, which could be a high-energy process. The potential profiles are shown in the following two figures.



For the dissociation starting from B state, the intersystem crossing with quartet state could bring the hot molecule down to the ground state through the intermediate D_1 state with in the planar C_s symmetry. All other internal conversion pathways in C_{2v} and twisted C_s symmetry have high-energy requirements that could not be reached by the laser energy used in the experiment. The corresponding potential energy profiles are shown in the following two figures.



The current results are being written as a full paper, and will be finished soon.

j. Photodissociation of formaldehyde (H_2CO)

For this project, from *ab initio* potential energy surfaces calculations we have not found any direct pathways, through which the molecule could jump onto ground state and dissociate into molecular product. Last time, we proposed that the S_1 and T_1 cumulated transition probability could lead the S_1 molecule jump onto T_1 state and then move onto S0 state through the S_0 and T_0 intersystem crossing. To verify this proposed mechanism, we planed to run direct semicalssical nonadiabatic dynamic. To keep conservation principle of energy and momentum, the velocity of the nuclei has to be adjusted after the singlet and triplet transition, however, we have not derived a suitable theory to describe situation induced by the interaction between orbital angular momentum and nuclear spin. To solve the problem, one way is still to develop a set of theories to describe this situation; the other way is to construct the potential energy

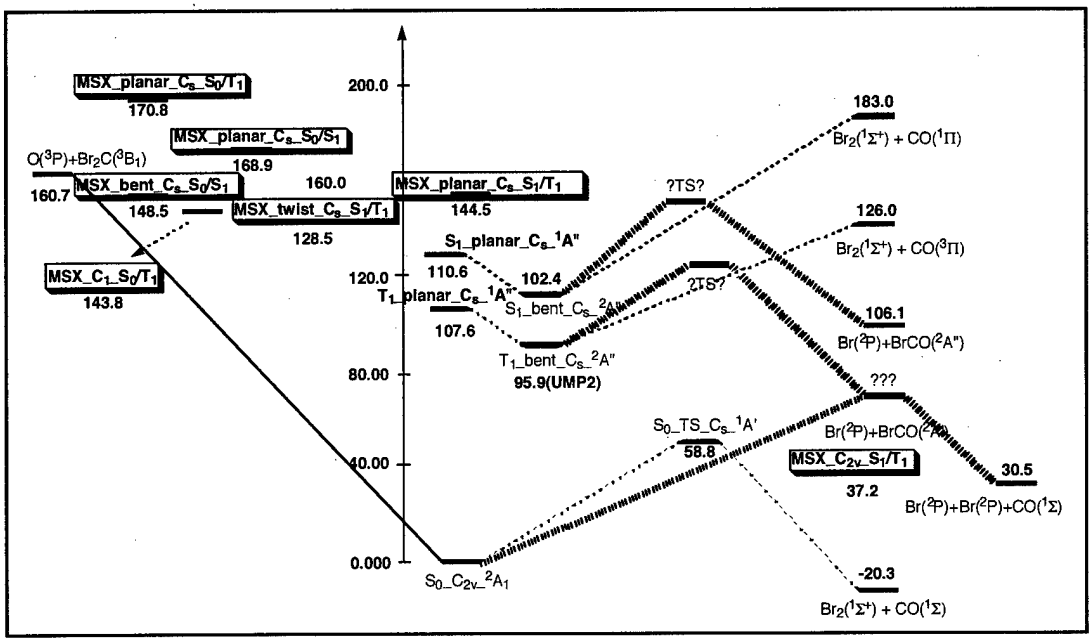
surfaces, diabatize them and run dynamics on the diabatized surface. We are continuing working on this problem in both directions.

k. Photodissociation of Carbonyl Dibromide (Br_2CO)

Emission of bromine-containing species into the atmosphere has raised concern regarding their potential impact on stratospheric ozone abundances. Bromine released from these species in the form of bromine atoms play a significant role in the bromine catalytic cycle for ozone removal. Carbonyl dibromide was shown to be produced in the atmosphere, concerning its photodissociation, recently, Francisco's group reported the new results on the photodissociation mechanism of CBr_2O at 267 nm using ion velocity imaging and time-of-flight mass spectrometry methods. Both molecular elimination (Br_2 + CO) and atom (Br) elimination pathways were found in the experiments.

Since molecular elimination products cannot correlate to the excited state, nonadiabatic effect must play a significant role in this reaction of A state. The present research is trying to calculate the potential energy surfaces involved in the reaction and to provide a qualitative explanation of the experimentally observed mechanism as well as the dynamic features, such as the angular factor. We have used the CASSCF(18e/14o) (ECP basis set for Br atom and cc-pVDZ basis set for C and O ayoms) method for geometry optimization of the equilibrium, transition state, product for both S_0, S_1 and T_1 states and the seam of crossing between them.

The present results are shown in Figure 2. These results indicate that both in planar Cs and non-planar Cs symmetry S_0 and S_1 state can cross with the C-O bond stretch. However, both of the channels are not energetically favored.(the energy of the seam of crossing is higher than the photon excitation energy) We also found that S_1 and T_1 can cross at several regions. For instance, S_1 and T_1 cross in the C_{2v} symmetry, and this a low energy pathway. Through this way, the molecule would move from S_1 to T_1 with C-O stretch and dissociate to produce the atom products, which agrees with the experiments. Peng Zhang, a graduate student, is running this project, and we plan to continue our study on trajectory calculation and provide deep insights into this reaction.



C. Other Elementary Reactions

a. Mechanisms of the reactions of alkyl bromides with O (^{3}P) atoms

Gas-phase atmospheric reactions of halogen compounds are of interest due to their possible role in ozone depletion, where halogens such as bromine and iodine may play a role analogous to that of chlorine in catalytic cycles that destroy ozone. Recent experimental research has investigated the kinetics and mechanisms of such reactions. In addition, *ab initio* electronic structure methods have provided thermochemical and mechanistic information for reactions involving iodide compounds.

Much of this current experimental and theoretical research has explored the gas-phase reactions of alkyl iodides with O (^{3}P) atoms. These reactions include a "spin-allowed" reaction producing OI and alkyl radicals

1a) $O(^3P) + IC_nH_{2n+1} \rightarrow OI(^2\Pi) + C_nH_{2n+1}$

and a "spin-forbidden" reaction producing HOI and an alkene

1b) $O(^3P) + IC_nH_{2n+1} \rightarrow HOI + C_nH_{2n}$

The reaction producing OI products may occur entirely on a triplet electronic potential energy surface of the $O(^3P) + IC_nH_{2n+1}$ "supermolecule". The "spin-forbidden" reaction 1b) may only occur via an intersystem crossing from a triplet to a singlet electronic state. In spite of this, experiments show significant branching to both channels for the reaction of oxygen with many alkyl iodides. Experimental results also show that HOI may be formed at very low collision energies. Results of collision experiments at varying impact energies suggest that OI is formed by two pathways. One is open at very low collision energies and the other is accessible at higher energies, in excess of approximately 8 kcal/mol. Molecular orbital calculations have recently elucidated the mechanisms of the reactions of CH_3I and C_2H_5I with oxygen. The results of the study of the C_2H_5I-O system corroborate the experimental results. Computations indicate that HOI and OI are likely to be formed at low energies via a singlet pathway accessible by an intersystem crossing, and that OI may also be formed by a second pathway on a triplet surface.

The analogous reactions of alkyl bromides, however, have not yet received a great deal of attention. A preliminary experimental study of collisions of 1,2-$C_2H_4Br_2$ with $O(^3P)$ at impact energies of approximately 12 kcal/mol show no reactions producing analogous OBr and HOBr products. This is remarkable in that reactions 1a) and 1b) are both observed under similar experimental conditions, as described above. While there have been some computational studies of the reactions of OBr and HOBr, there have been no previous theoretical investigations of the reactions of alkyl bromides with O atoms.

Here, we present such studies for the systems C_2H_5Br + O and 1,2-$C_2H_4Br_2$ + O; the reactions specifically studied are

2a) $C_2H_5Br + O\ (^3P) \rightarrow OBr + C_2H_5$

2b) $C_2H_5Br + O\ (^3P) \rightarrow HOBr + C_2H_4$

and their analogous reactions for the dibrominated alkane

3a) $C_2H_4Br_2 + O\ (^3P) \rightarrow OBr + C_2H_4Br$

3b) $C_2H_4Br_2 + O\ (^3P) \rightarrow HOBr + C_2H_3Br$

Ab initio electronic structure computations have been performed to study the singlet and triplet potential energy surfaces involved in the gas-phase reactions of O (^3P) with the alkyl bromides C_2H_5Br and 1,2-$C_2H_4Br_2$ to produce spin-allowed OBr and spin-forbidden HOBr products. The computations explore the effects of multiple alkane bromination on the reaction path. Our calculations indicate that high barriers to OBr formation exist on the triplet potential energy surface of alkyl-bromides reacting with O atoms. We compute spin-orbit couplings between the singlet and triplet surfaces at the lowest points where the surfaces intersect. We conclude that OBr products may be observed at sufficiently high collision energies via the triplet path while there is low probability of production of OBr or HOBr from a singlet state.

The present work was published as J. E. Stevens, M. S. Kaufman, and K. Morokuma, Molecular Orbital Study of Mechanisms of the Reactions of Alkyl Bromides with O (^3P) Atoms, J. Chem. Phys., **118**, 6964-6973 (2003).

b. Reaction Mechanism of NCl(a) + NCl(a) → Various Deactivation Channels

As a measure of CAIL efficiency, the concentration of the energy carrier species, NCl(a $^1\Delta_g$), needs to be maintained at high level. Unfortunately, high concentrations of this molecule will cause some self-annihilation by the pathways shown below.

NCl(a) + NCl(a) → NCl(b $^1\Sigma^+$) + NCl(X $^3\Sigma^-$)) (A)

→ NCl(a) + NCl(X) + E (~1eV in translation ,vibration) (B)

→ NCl(X) + NCl(X) + E(~2eV in translation ,vibration) (C)

Pathway (A) is called the "pooling" process during which ground and second excited NCl molecules are formed and little energy is released. The (B) and (C) channels also annihilate at least one NCl(a) molecule but also release heat in the form of fragment translation and vibration. Some experimental knowledge exists about the "pooling" channel, and little or no information is available about the other two channels. In order to investigate the unfavorable impact of these energy destruction processes, we have performed ab initio calculations for the interaction and reaction of two NCl(a) species.

A scan of the trans symmetric (C_{2h}) approach of the two NCl molecules in various electronic states shows clearly that there will be a crossing between the reactant state, NCl(a) + NCl(a), and the nearly

resonant NCl(b $^1\Sigma^+$) + NCl(X $^3\Sigma^-$) state at the N-N distance of approximately 2.8Å, with an energy only a few kcal/mol above the NCl(a) + NCl(a) reactant asymptote. A very similar situation is also found for the cis symmetric (C_{2v}) scan. Thus, the nonadiabatic transition through this crossing is expected to occur at low energy, but because of its spin-forbidden nature, is not expected to be a very efficient process. The geometry optimization and frequency calculation indicates that as two NCl(a) molecules approach closer, the $(NCl)_2$ will be twisted to a C_2 configuration.

This work has just been published G. S. Tschumper, M. C. Heaven and K. Morokuma, An ab initio Excursion on the Lowest 18 Electronic Surfaces of the NCl + NCl System: Some Insight into the Long-Range Self-Quenching Pathways of the First Excited State of NCl, J. Phys. Chem. A, **106,** ASAP (2002).

c. The Stability of Dichlorodiazene

The stability of the weak van der Waals complex of $(NCl)_2$, also know as dichlorodiazene, ClN=NCl, has been studied with high level ab initio methods. Triple-zeta basis sets with d and f polarization functions are required to obtain even qualitative agreement between multi-reference and highly-correlated single reference electronic structure methods concerning the stability of cis- and trans-ClN=NCl with respect to dissociation to $N_2$and 2Cl. The CCCSD(T) method predicts a barrier to dissociation of 7-8 kca/mol for the two isomers. CASPT2 barrier heights are substantially smaller (<1.5 kcal/mol) and suggest that these species are barely bound. The present work has been published as G. S. Tchumper, M C. Heaevn and K. Morokuma, Concerning the Stability of Dichlorodiazene, Chem. Phys. Lett., **370,** 418-424 (2003).

d. Dipole moments of highly vibrationally excited HCN.

Vibrational state specific dipole moments are diagnostic of the degree of localization of vibrational states in highly vibrationally excited HCN. Using a newly calculated global ab initio dipole moment function and previously calculated highly accurate vibrational wave functions, we show that delocalized (i.e. isomerizing) vibrational states of HCN possess markedly lower dipole moments than localized HCN or HNC states. We also show that the vibrational quantum number dependence of the dipole moment can be used to distinguish delocalized states from localized Franck-Condon-dark states that are made observable by perturbations with localized Franck-Condon-bright states. Furthermore, using classical trajectory analysis we introduce and describe a new experimental approach to obtain these data, which relies on combining optical pumping and state specific molecular transport with hexapoles. With this method it is possible to determine state specific dipole moments with high accuracy and precision.

This work has just been published as J. M. Bowman, S. Irle, K. Morokuma, and A. Wodtke, Dipole moments of highly vibrationally excited HCN: theoretical prediction of an experimental diagnostic for delocalized states. J. Chem. Phys., **114**, 7923-7934 (2001).

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P. Zhang, G. S. Tschumper, S. Irle and K. Morokuma, Ab initio theoretical studies of potential energy surfaces for the photodissociation of the vinyl radical. I. $\tilde{A}$ state dissociation, J. Chem. Phys., 119, 6524-6538 (2003).

4. Interactions/Transactions.

Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories.

1. We have been in close contact with Dr. Viggiano and Dr. Williams of the Air Force Research Laboratory at the Hanscom Air Force Base concerning the interpretation of their ion-molecule experimental results.

2. We have been in close contact with Drs. Dressler of the Air Force Research Laboratory at the

Hanscom Air Force Base, concerning the interpretation of the experimental results for their ion-molecule and other reaction system.

5. New inventions and patent disclosures.

None.

6. Honors/Awards.

The President of the International Academy of Quantum Molecular Science. (This is an organization of about 85 prominent molecular quantum scientists in the world, that include six Nobel Prize winners in Chemistry and Physics.) Served for July 2000 – July 2003, and reelected for another 3-year term for July 2003 - July 2006 .

Elected in 2003 as Fellow, American Association for the Advancement of Science.

Listed in top 50 most cited scientists in chemistry for January 1993 - June 30, 2003. http://www.in-cites.com/nobel/2003-che-top100.html